



# Double-edged sword effects of cation rotation and additive passivation on perovskite solar cell performance: an ab initio investigation



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## ABSTRACT

Perovskite solar cells, mainly based on the prototypical  $\text{CH}_3\text{NH}_3\text{PbI}_3$ , have recently emerged as a disruptive technology in the solar cell industry. Despite the great successes in the exceptional power conversion efficiency, many underlying mechanisms involving the structures and performance of the perovskite solar cells remain elusive, such as the role of the methylammonium cation and the optimization of the passivation technique. These hinder the formulation of a universal design principle that can guide us to rationally improve the perovskite solar cell performance. In addition, the notorious stability issue in perovskite solar cells prevents the solar cell from wide industrial application. In this manuscript, we closely examine the cation rotation and the passivating layer at the halide perovskite surface in the context of the stability issue. An experimentally-proved passivating agent iodopentafluorobenzene (IPFB) is used as an example. The ab initio investigation is performed via constraining/relaxing the cation rotation at the perovskite surface and manipulating the coverage of IPFB. Many existing reports tend to agree that the methylammonium cation rotation could be beneficial to the outstanding performance of the perovskite solar cell due to the ferroelectric effect. On the other hand, the passivating agents such as molecular additives tend to universally improve the device stability. In this study, our calculation suggests that: 1) the methylammonium cation rotation could undesirably accelerate the water infiltration process at the perovskite surface; 2) the passivating layer can counter-intuitively facilitate the water interaction with the perovskite surface; both of these could severely degrade the solar cell stability. Therefore, we emphasize on the double-edged sword effects of cation rotation and additive passivation on the stability of the perovskite solar cells. This study facilitates the convergence to the fundamental understanding of the organic-inorganic perovskite solar cells and is beneficial for the rational design of the halide perovskite-based optoelectronic devices.

## 1. Introduction

Recent years have witness a rapid development of the perovskite solar cells, with the highest power conversion efficiency (PCE) overpassing 22%, demonstrating potentials to disrupt the solar cell industry [1–7]. Perovskite solar cells are functionalized by a halide perovskite light absorber, usually based on the prototypical  $\text{CH}_3\text{NH}_3\text{PbI}_3$  material, which consists of a PbI framework and a methylammonium cation that can freely rotate inside a PbI cavity [8–11]. Despite of enjoying the excellent PCE that is comparable to the silicon solar cells, the perovskite solar cells have a number of issues that remain to be solved before large scale fabrication and industrial application [12–14].

One of the major drawbacks of perovskite solar cells is their stability issue, since the halide perovskite material is sensitive to water

molecules and oxygen in the atmosphere, which degrade the perovskite layer and detriments the solar cell overall performance [15–17]. The water adsorption and degradation is initiated at the perovskite surfaces, and many efforts have been spent to engineer the perovskite surface/interface to retard water adsorption and further penetration [18]. One of the very efficient routes is to include a passivating layer on top of the perovskite surface [19,20]. In particular, researchers have employed molecular additives to passivate the perovskite surfaces and interfaces such as those based on Lewis base and halogen bond interactions and improve the device water stability [21–26]. Nevertheless, many aspects of the surface/interface additives working mechanisms are poorly understood, for instance some similar additive structures and synthetic routes might leads to vastly different device performance that cannot be well explained [27–29]. There is a lack of coherent design principle to

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effectively engineer the perovskite surfaces/interfaces; the quest to find an optimal and champion passivating material that can efficiently improve the perovskite solar cell performance is appealing, and the success could be much reliant on the understanding of the structures and properties of the passivating layer/perovskite system. Efforts should be spent on elucidating the mechanisms of passivating layer effects on the perovskite solar cell performance.

Many more questions about the halide perovskite material are waiting to be justified, for example the exact role of the molecular cation rotation in the halide perovskite layer [30–32]. The cation, usually composed of methylammonium, is disordered and dynamically moving in the halide perovskite crystal structure [33–35]. Many experiments and calculations suggest that the methylammonium can freely rotate at the room temperature, with a time constant as small as several picoseconds [35–37]. The free rotation of the cation is suggested to be associated with the domain wall configuration and ferroelectricity, which might lead to efficient charge carrier transport and outstanding optoelectronic properties of the solar cell [36,38,39]. As a result, the methylammonium rotation is generally considered to be benign [35,40–42].

In this manuscript, we investigate the cation rotation and passivating layer effects on the halide perovskite surface structures and properties, and determine the water penetration barrier at the perovskite surface with variable cation rotation constraints and different passivating layer structures to evaluate the cation rotation and passivation effects on the  $\text{CH}_3\text{NH}_3\text{PbI}_3$  water stability. Interestingly, we find that the cation rotation and the passivating layer could be detrimental to the solar cell performance. An experimentally-proved passivating agent iodopentafluorobenzene (IPFB) with different surface coverage is employed as an example to understand the perovskite surface passivation effects [43,44]. IPFB can adsorb onto the perovskite surface via the halogen bond between the halogen atom in the molecule and the halogen atom at the perovskite surface. The cation is either fixed or relaxed to better understand the cation rotation effects on the perovskite stability issue. The detailed electronic/optical properties of the perovskite surfaces are explained via the calculation of the projected density of states (PDOS) spectra and UV–vis light absorption spectra in the presence of water.

## 2. Computational details

Geometrical optimization of the bare and passivated halide perovskite surface is performed using the PBE functional in Dmol3 [45], with all electrons treated at the relativistic and DND level. The (001) surface direction is focused since this has been proved to be one of the most stable surfaces in  $\text{CH}_3\text{NH}_3\text{PbI}_3$  from a number of studies [18,46,47]. Many surface terminations have been proposed to exist in  $\text{CH}_3\text{NH}_3\text{PbI}_3$ , while the cation-terminated perovskite surface is selected in this study since the passivation of the IPFB molecules has been suggested to be mainly available the cation-terminated surface [43,44], while the PbI-terminated surface could present self-passivation effects that complicates the theoretical modeling procedure in this study [48]. A 20 Å vacuum layer is inserted into the unit cell to avoid the unnecessary interlayer interactions. The bottommost layer is fixed during the geometrical relaxation step to mimic better the real scenario where the perovskite surface lattices are constrained by the bulk perovskite crystal [49,50].

In order to comprehensively understand the perovskite surface cation rotation effects, four types of perovskite surfaces depending on whether the cation is fixed or relaxed (**Method 1–4**) are prepared. **Method 1** corresponds to the relaxation method where all the layers are relaxed; **Method 2** corresponds to the relaxation method where only the methylammonium cations are allowed to rotate while the PbI framework is fixed; **Method 3** corresponds to the relaxation method where the methylammonium cation are fixed while the PbI framework is allowed to relax; **Method 4** corresponds to the relaxation method

where all the layers are fixed. The breakdown into the four methods allows us to comprehensively understanding the perovskite surface cation rotation effects. For each method, a water molecule is put on top of the perovskite surface at a random position as the starting point before geometrical optimization. The energy barriers of water penetration at the perovskite surface, with different penetration depths are determined using the complete LST/QST method at the PBE level. Starting from the initial water molecular adsorption, three optimized geometries A, C and E with increasing water penetration depths are obtained (Fig. S1). The transition state between A and C is termed B, while the transition state between C and E is termed D. Further penetration of water is not probed since the lattice constraint effect hinders the movement significantly. [51,52]

In order to understand the perovskite surface passivation effects, four perovskite surface systems (0H, 1H, 2H and 3H) passivated with increasing degrees of coverage are prepared to identify the water penetration barriers at different passivating additive coverage. 0H corresponds to no additive in the unit cell; 1H corresponds to one molecular additive in the unit cell; 2H corresponds to two additives in the unit cell; 3H corresponds to three additives in the unit cell. 4H corresponds to four additives in the unit cell. For each degree of the passivation coverage, four optimized water/perovskite systems (with increasing water penetration depth: M, A, C and E) are identified. The transition state between M and A is termed N; the transition state between A and C is termed B; the transition state between C and E is termed D. The corresponding regions of the water molecules in M, N, A, B, C, D and E are depicted in Fig. S1. A refers to the state where the water molecule for first time starts to adsorb stably onto the bare perovskite surface (the yellow region in Fig. S1). C refers to the state where the water molecule resides stably in the uppermost PbI cavity in the bare perovskite system (the red region in Fig. S1). E refers to the stable state where the water molecule penetrate deeper into the PbI underlayer in the bare perovskite system (the blue region in Fig. S1) M refers to the state where the water molecule reside stably on top of the IPFB molecule in the IPFB-passivated perovskite system (the purple region in Fig. S1). B refers to the transition state between A and C. D refers to the transition state between C and E. For the halogen capped perovskite systems, additional states M and N are introduced. N refers to the transition state between M and A. Based on the optimized structure, a  $4 \times 4 \times 1$  sampling is employed to obtain the PDOS spectra while a  $3 \times 3 \times 1$  k-point set is used to calculate the optical properties in CASTEP. [53]

## 3. Results and discussion

Relative energies (eV) of structures A, B, C, D and E obtained from **Method 1–4**, and the corresponding structures are demonstrated in Fig. 1. The energy barrier is predicted to be 0.31 eV from A to C calculated via **Method 1**, while the energy barrier is 0.52 eV from A to C using **Method 3**. Since **Method 1** and **Method 2** only differ by the fixation or relaxation of the methylammonium cation, the energy barrier difference show that the methylammonium free rotation induces a 0.46 eV (the difference between 0.77 eV and 0.31 eV) decrease in the water infiltration energy barrier into the perovskite surface. As a result, the free rotation of the methylammonium cation leads to an easier water infiltration into the halide perovskite surface. In addition, the energy barrier increases by 0.55 eV (the difference between 0.86 eV and 0.31 eV) when all the cation and PbI framework are constrained, while the energy barrier increases by 0.21 eV (the difference between 0.52 eV and 0.31 eV) when PbI framework is fixed while the cation is relaxed. These demonstrate both cation rotation and PbI framework movement can result in easier water infiltration. By separately considering the contribution from cation relaxation and the PbI framework relaxation, the decomposition of different factors on the water infiltration energy barrier can be understood. From C to E, the energy barriers are 1.03 eV, 0.95 eV, 0.54 eV and 4.27 eV respectively calculated via **Method 1–4**.

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